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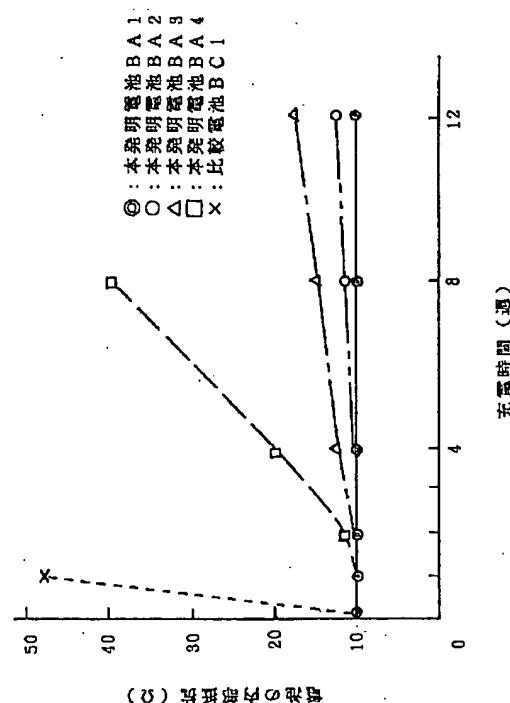
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(54)【発明の名称】 非水系電解質二次電池

(57)【要約】

【構成】リチウム金属、又は、リチウムを吸収放出可能な物質を主材とする負極と、組成式 $Li_xMe_yMnO_z$  ( $Me$ は $B$ 、 $Si$ 、 $P$ 、 $Ga$ 、 $Ge$ 、 $As$ 、 $Se$ 、 $In$ 、 $Sn$ 、 $Sb$ 、 $Te$ 、 $Pb$ 、 $Po$ 及び $At$ よりなる群から選ばれた少なくとも一種の元素;  $x$ 、 $y$ 及び $z$ は正数)で表される複合酸化物を活性物質とする正極とを備えてなる。

【効果】特定の複合酸化物を活性物質とする正極が使用されているので、充電の際に複合酸化物中に含まれるマンガンの非水系電解質中の溶出が起こりにくく、内部抵抗の上昇が殆ど起こらない。それゆえ、本発明電池は高率放電特性に優れる。



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# PATENT ABSTRACTS OF JAPAN

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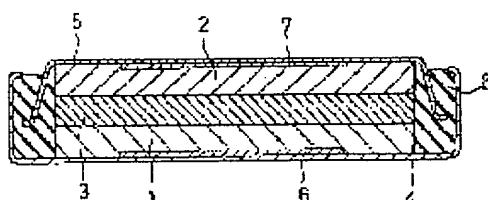
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## (54) NONAQUEOUS ELECTROLYTE SECONDARY BATTERY

### (57)Abstract:

PURPOSE: To prevent the elution of manganese included in the compound oxide into the nonaqueous electrolyte at the time of charge, and prevent the rise of the inner resistance to obtain the high efficient discharge characteristic by using a positive electrode, in which a specified compound oxide is used as active material.

CONSTITUTION: This nonaqueous electrolyte secondary battery is provided with a negative electrode 2 mainly composed of lithium metal or the material, which can store and discharge lithium, and a positive electrode 1, in which a compound oxide expressed by a composition formula  $LiXMe_yMnO_z$  (Me means at least one kind of element selected among the group of B, Si, P, Ga, Ge, As, Se, In, Sn, Sb, Te, Pb, Po and At; x, y and z means positive number) is used as active material.



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## CLAIMS

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### [Claim(s)]

[Claim 1] The nonaqueous electrolyte rechargeable battery characterized by coming to have the negative electrode which uses as a principal member a lithium metal or the matter which can occlusion emit a lithium, and the positive electrode which uses as an active material the multiple oxide expressed with an empirical formula  $LiX Mey MnOZ$  (a kind of element; x [ at least ] chosen from the group which Me becomes from B, Si, P, Ga, germanium, As, Se, In, Sn, Sb, Te, Pb, Po, and At, and y and z are a positive number).

[Claim 2] Said empirical formula  $LiX Mey MnOZ$  inner y is a nonaqueous electrolyte rechargeable battery according to claim 1 which are 0.04 or more and 1.0 or less.

[Claim 3] Said empirical formula  $LiX Mey MnOZ$  It is the nonaqueous electrolyte rechargeable battery according to claim 1 whose y inner Me is B and is 0.04 or more and 1.0 or less.

[Claim 4] Said multiple oxide is  $Li_2 B_4 O_7$  expressed with an empirical formula  $LiX By MnOZ$  ( $0.04 \leq y \leq 1.0$ ). Nonaqueous electrolyte rechargeable battery according to claim 1 which is a content multiple oxide.

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## DETAILED DESCRIPTION

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### [Detailed Description of the Invention]

#### [0001]

[Industrial Application] Especially this invention relates to amelioration of the elution-proof nature to the nonaqueous electrolyte of the manganese contained in manganese content positive active material with respect to a nonaqueous electrolyte rechargeable battery.

#### [0002]

[Description of the Prior Art] In order to attain high capacity-ization in a nonaqueous electrolyte rechargeable battery in recent years, it is  $Li_2 MnO_3$  as positive active material. The manganese (spinel) content multiple oxide of content  $MnO_2$  (refer to JP,63-114064,A), the Li content  $MnO_2$  (refer to JP,1-235158,A),  $LiMn_2O_4$ , etc. is proposed.

[0003] By the way, in order to attain that high capacity-ization actually in the case of this kind of nonaqueous electrolyte rechargeable battery, it is necessary to charge until a positive electrode becomes remarkable high potential (it is [ as opposed to / usually /  $Li^+/Li$  single electrode potential ] beyond about 3.6V).

[0004] However, if it charges until a positive electrode becomes high potential such, the manganese in a manganese content multiple oxide will be eluted in an electrolyte, the internal resistance of a cell will become large, and it will become difficult to be able to bear the big discharge current, namely, to obtain the cell excellent in the high-rate-discharge property.

[0005] The elution to the inside of the electrolyte of manganese hardly happens, but the place which this invention is made in order to solve this problem, and is made into the

purpose has it in offering the nonaqueous electrolyte rechargeable battery which was so excellent in the small high-rate-discharge property of a rise of internal resistance, when it charges until a positive electrode becomes remarkable high potential, in order to enlarge cell capacity.

[0006]

[Means for Solving the Problem] The nonaqueous electrolyte rechargeable battery (the "this invention cell" is called hereafter.) concerning this invention for attaining the above-mentioned purpose A lithium metal, or the negative electrode which uses as a principal member the matter which can occlusion emit a lithium and an empirical formula  $LiX$   $Mey MnOZ$  ( $Me$  --  $B$  --) At least a kind of element chosen from the group which consists of Si, P, Ga, germanium, As, Se, In, Sn, Sb, Te, Pb, Po, and At;  $x$ , and  $y$  and  $z$  come to have the positive electrode which uses as an active material the multiple oxide expressed with a positive number.

[0007] Positive-active-material slack empirical formula  $LiX$   $Mey MnOZ$  in this invention cell Although the value of the atomic ratio of  $Me:Mn$ , i.e., the value of  $y$  in an empirical formula, can use various things as a multiple oxide expressed, since that the value of  $y$  uses the thing of 0.04-1.0 can stop the elution to the inside of the electrolyte of manganese effectively and it can control the rise of the internal resistance of a cell sharply as shown also in the example mentioned later, it is desirable. That is, since elution depressor effect of the manganese according to increase in quantity of the addition of  $Me$  not only can hardly expect, but the discharge capacity as positive active material of the multiple oxide concerned falls even if the elution depressor effect of manganese according that the value of  $y$  is less than 0.04 to compound-izing with  $Me$  compound and a manganese content multiple oxide is not fully discovered but the value of  $y$  exceeds 1.0 on the other hand, since the addition of  $Me$  is not enough, it is not [ both ] desirable.

[0008]  $LiX$   $Mey MnOZ$  in this invention The positive electrode used as an active material is obtained as follows, for example. First, a lithium hydroxide ( $LiOH$ ), 3 oxidation 2 boron ( $B-2 O_3$ ), and a manganese dioxide ( $MnO_2$ ) are heat-treated at 250-1000-degree about C temperature for about 20 hours, after mixing by the predetermined mole ratio.

[0009] subsequently, binders, such as electric conduction agents, such as acetylene black if the active material which carried out in this way and was obtained is required, after grinding it to a predetermined particle size, and carbon black, and polytetrafluoroethylene (PTFE), and poly vinylidene fluoride (PVdF), -- usually -- a weight ratio -- about 80 to 90:5 to 15:4 to 15 ratio -- mixing -- a positive electrode -- it considers as a mixture.

[0010] furthermore, this positive electrode -- pressurization molding of the mixture is carried out by the predetermined pressure (usually 0.5-1.5t/cm<sup>2</sup>), obtained molding is rolled out and heat-treated to the mesh-like disk made from the stainless steel as a charge collector etc. (it usually heats about [ 100-250 degrees ] by C), and it considers as a positive electrode.

[0011] The negative electrode in this invention cell is constituted considering the matter which can occlusion emit a lithium metal or a lithium as a principal member. When using a lithium metal, predetermined dimension configurations, such as disc-like, are processed by rolling, punching, etc., and use is presented.

[0012] As matter which can occlusion emit a lithium, carbon materials, such as a lithium alloy, and a graphite, corks, are illustrated. When using powdered matter, such as a

carbon material this, a binder, and the need -- responding -- an electric conduction agent -- usually -- a weight ratio -- about 80 to 90:5 to 15:4 to ten ratio -- mixing -- a negative electrode, after considering as a mixture this negative electrode -- pressurization molding of the mixture is carried out by the predetermined pressure (usually 0.5-1.5t/cm<sup>2</sup>), obtained molding is rolled out and heat-treated to the mesh-like disk as a charge collector etc. (it usually heats about [ 100-250 degrees ] by C), and it considers as a negative electrode.

[0013] In the nonaqueous electrolyte rechargeable battery with which it comes to use the matter [ this invention cell ] like \*\*\*\* which can occlusion emit a lithium metal and a lithium as a principal member of a negative electrode It is what has the greatest description at the point that the specific multiple oxide is used as positive active material. So, it is possible to use the various ingredients which are conventionally used as an object for nonaqueous electrolyte rechargeable batteries, or are proposed about the member of others, such as a nonaqueous electrolyte and a separator (when using a liquid electrolyte). [0014]

[Function] In this invention cell, since the specific manganese content multiple oxide is used as positive active material, even if a positive electrode is exposed to high potential at the time of charge for high-capacity-izing, elution to the inside of the electrolyte of the manganese contained in a manganese content multiple oxide cannot happen easily, and internal resistance of a cell cannot rise easily.

[0015]

[Example] It is possible to change this invention suitably in the range which is not limited at all by the following example and does not change the summary, and to carry out hereafter, although this invention is further explained to a detail based on an example.

[0016] (Examples 1-4)

[Production of a positive electrode] A lithium hydroxide (LiOH) and 3 oxidation 2 boron (B-2 O<sub>3</sub>), The atomic ratio of Li:B:Mn a manganese dioxide (MnO<sub>2</sub>), respectively 0.58:0.16:1.00 (example 1), After mixing so that it may be set to 0.54:0.08:1.00 (example 2), 0.52:0.04:1.00 (example 3), and 0.51:0.02:1.00 (example 4), it heat-treated by 850-degreeC for 20 hours, and the positive active material of the shape of four sorts of powder was obtained. When the positive active material of the shape of these powder was investigated with the X-ray diffraction method, respectively, it is LiMn<sub>2</sub>O<sub>4</sub>. And Li<sub>2</sub>B<sub>4</sub>O<sub>7</sub> Existence was checked.

[0017] subsequently, such positive active material -- the acetylene black as an electric conduction agent and the fluororesin powder as a binder, and the weight ratio 90:6:4 -- mixing -- four sorts of positive electrodes -- the mixture was obtained.

[0018] furthermore, these positive electrodes -- a mixture -- respectively -- 2 t/cm<sup>2</sup> The molding obtained by disc-like [ with a diameter of 20mm ] by carrying out pressurization molding was rolled out to the mesh-like disk made from the stainless steel as a charge collector by the pressure, it heat-treated under the 2-hour vacuum by 250-degreeC, and four sorts of positive electrodes were produced.

[0019] [Production of a negative electrode] The disc-like negative electrode which consists of a lithium metal with a diameter of 20mm was produced by rolling and punching.

[0020] [Preparation of a nonaqueous electrolyte] One mol /of lithium perchlorates was melted 1. to the mixed solvent of the volume ratio 1:1 of propylene carbonate and 1 and 2-

dimethoxyethane, and the nonaqueous electrolyte was prepared to it.

[0021] [Production of a nonaqueous electrolyte rechargeable battery] The positive-electrode can besides the above-mentioned positive/negative two poles and a nonaqueous electrolyte, the negative-electrode can, etc. were used, and the nonaqueous electrolyte rechargeable batteries BA1 (example 1), BA2 (example 2), BA3 (example 3), and BA4 (example 4) (each cell dimension is diameter:24mm and thickness:3mm) of the flat mold concerning this invention were produced. In addition, as a separator, the microporous thin film made from polypropylene was used, and the nonaqueous electrolyte described above to this was infiltrated.

[0022] Drawing 1 is the sectional view of the produced cell BA 1 (the same is said of cells BA2-BA4), and the cell BA 1 shown in this drawing consists of a positive electrode 1, a negative electrode 2, a separator 3, the positive-electrode can 4, the negative-electrode can 5, the positive-electrode charge collector 6, a negative-electrode charge collector 7, insulating packing 8 made from polypropylene, etc. The chemical energy which holds in the cell case which a positive electrode 1 and a negative electrode 2 counter through a separator 3, and the positive/negative two-poles cans 4 and 5 form, and the negative electrode 2 was connected to the positive-electrode can 4 for the positive electrode 1 through [ again ] the negative-electrode charge collector 7 at the negative-electrode can 5 through the positive-electrode charge collector 6, and was produced in the cell BA1 interior can be taken out now to the exterior as electrical energy from the both-ends child of the positive-electrode can 4 and the negative-electrode can 5.

[0023] (Example 1 of a comparison) In production of a positive electrode, 3 oxidization 2 boron was not blended but the comparison cell BC 1 was produced like the example 1 except the atomic ratio of Li:Mn having mixed the lithium hydroxide (LiOH) and the manganese dioxide (MnO<sub>2</sub>) so that it might be set to 0.5:1.0.

[0024] About the comparison cell BC 1 produced in the cells BA1-BA4 and the example 1 of a comparison which were produced in the examples 1-4, the relation between the charging time at the time of charging continuously and the internal resistance of a cell was investigated by charge electrical-potential-difference 4.0V fixed. A result is shown in drawing 2 .

[0025] Moreover, it is the graph which took and expressed the charging time (week) with the axis of abscissa. drawing 2 -- an axis of ordinate -- the internal resistance (omega) of a cell -- O among this graph A cell BA 1 (Mn:B=1.00:0.16;y=0.16) O A cell BA 2 (Mn:B=1.00:0.08;y=0.08) In \*\*, a cell BA 3 (Mn:B=1.00:0.04;y=0.04) and \*\* show a cell BA 4 (Mn:B=1.00:0.02;y=0.02), and x shows the result about the comparison cell BC 1 (boron combination is not carried out), respectively.

[0026] Multiple oxide LiX By MnO<sub>2</sub> which contains boron from this graph The used cells BA1-BA4 are understood that the rise of the internal resistance accompanying advance of charge is small compared with the comparison cell BC 1 which used the multiple oxide which does not contain boron. LiX By MnO<sub>2</sub> whose value of y is 0.04 or more especially By the cells BA1-BA3 used as positive active material, it turns out that the rise of internal resistance is controlled notably.

[0027] In addition, when internal resistance disassembled the comparison cell BC 1 (the internal resistance one week after starting charge is 48ohms) which went up exceeding 20 ohms and ICP analysis investigated the negative electrode, it turned out that a lot of Mn deposits in the negative electrode. Moreover, although investigated also about the

negative electrode of the cells BA1-BA3 whose internal resistance 12 weeks after making it the same is 18ohms or less, the deposit of this Mn was not accepted.

[0028] It replaces with boron (B). Silicon (Si) Lynn (P), (Examples 5-56) A gallium (Ga), germanium (germanium), an arsenic (As), a selenium (Se), An indium (In), tin (Sn), antimony (Sb), a tellurium (Te), lead (Pb), a polonium (Po), Or except having used the astatine (At) as an alloying element, the nonaqueous electrolyte cell by which 52 sorts of positive active material differs was produced like examples 1-4, and the internal resistance of the cell in the time of eight weeks passing after charge initiation about each of these cells was measured. In addition, the atomic ratio of Li:Me(each alloying element):Mn was set to 0.5 (y+1):y:1.

[0029] A result is shown in Table 1. In this table, the internal resistance in the time of eight weeks passing after charge initiation of the comparison cell BC 1 produced in the cells BA1-BA4 and the example 1 of a comparison which were produced in the examples 1-4 is also written together. However, it replaces with an internal resistance value about the cell which exceeded 50 ohms before eight-week progress, and x has shown.

[0030]

[Table 1]

添加元素	マンガン1に対する各添加元素の原子比			
	0. 0 2	0. 0 4	0. 0 8	0. 1 6
B	4 0	1 5	1 1	1 0
S i	×	1 8	1 6	1 5
P	×	1 6	1 6	1 4
G a	×	1 4	1 4	1 2
G e	×	1 8	1 4	1 4
A s	×	1 6	1 6	1 4
S e	×	1 6	1 4	1 4
I n	×	1 6	1 4	1 4
S n	×	1 6	1 6	1 6
S b	×	1 8	1 6	1 4
T e	×	1 8	1 6	1 6
P b	×	1 8	1 8	1 6
P o	×	1 8	1 8	1 6
A t	×	1 8	1 3	1 1
無添加	×			

単位 :  $\Omega$

[0031] (Examples 57-112) Except having replaced heat-treatment temperature with 850-degreeC, and having been referred to as 375-degreeC, like examples 1-56, the nonaqueous electrolyte cell by which 56 sorts of positive active material differs was produced, and the internal resistance of the cell in the time of eight weeks passing after charge initiation about each of these cells was measured, respectively. In addition, the atomic ratio of Li:Me(each alloying element):Mn was set to 0.5 (y+1):y:1.

[0032] A result is shown in Table 2. However, about the cell which exceeded 50 ohms before eight-week progress, it replaces with an internal resistance value like Table 1, and x has shown.

[0033]

[Table 2]

添加元素	マンガン1に対する各添加元素の原子比			
	0. 0 2	0. 0 4	0. 0 8	0. 1 6
B	3 5	1 6	1 2	1 2
S i	4 5	1 8	1 2	1 2
P	3 5	1 8	1 2	1 2
G a	3 8	1 8	1 6	1 6
G e	3 6	1 8	1 6	1 6
A s	4 8	1 6	1 4	1 2
S e	3 6	1 8	1 4	1 4
I n	4 2	1 8	1 6	1 4
S n	4 4	1 8	1 8	1 6
S b	×	1 8	1 8	1 6
T e	×	1 8	1 6	1 6
P b	×	1 8	1 8	1 8
P o	×	1 8	1 6	1 6
A t	×	1 8	1 6	1 6
無添加	x			

単位 :  $\Omega$

[0034] From Table 1 and 2, this invention cell is compared with the comparison cell BC 1, and is understood that the rise of the internal resistance in the time of eight weeks passing is small. Moreover, LiX Mey MnOz whose value of y is 0.04 or more especially In the cell used as positive active material, it turns out that the rise of internal resistance is controlled notably.

[0035] Although the above-stated example explained the example in the case of applying this invention to a flat mold cell, there is especially no limit in the configuration of a cell, and this invention can be applied to the nonaqueous electrolyte rechargeable battery of various configurations, such as cylindrical and a square shape.

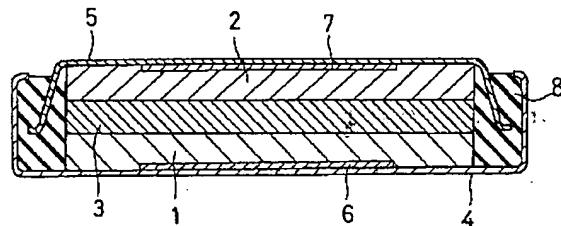
[0036]

[Effect of the Invention] In this invention cell, since the positive electrode which uses a specific multiple oxide as an active material is used, elution to the inside of the nonaqueous electrolyte of the manganese contained in a multiple oxide in the case of

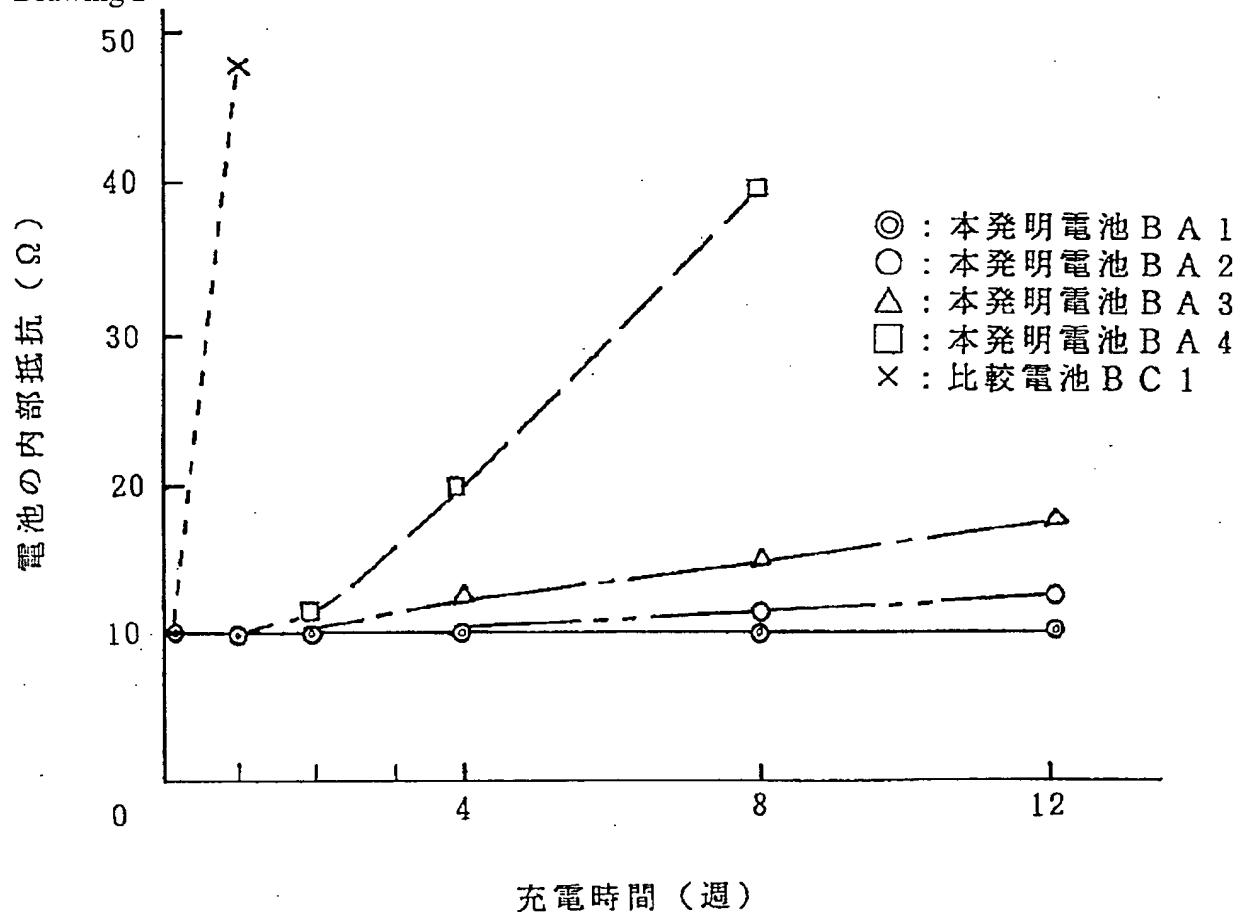
charge cannot happen easily, and the rise of internal resistance hardly takes place. So, this invention does the outstanding characteristic effectiveness -- this invention cell is excellent in a high-rate-discharge property.

Drawing 1

B A 1



Drawing 2



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